**FINAL REPORT—PHOTOASSISTED ELECTRON
TRANSFER REACTIONS OF APPLICATION
TO MINE WASTEWATER CLEANUP:
NITRATE AND CYANIDE**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 3**

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Final Report—Photoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Nitrate and Cyanide

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Foreword

Today industries are attempting to develop and modify their existing operations to manufacture products with environmentally safe technologies. Wastes generated by these industries are often unsightly and can threaten public health as well as degrade the environment, especially if they are left untreated or are improperly treated. Mine wastes are particularly suspect because of the presence of "mobile toxic constituents" (such as cyanide) that remain in tailings ponds and heap leach pads or acid mine drainage that contains heavy metals leached from sulfide minerals in exposed ore bodies.

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and nature's ability to support and nurture life. Such laws direct the EPA to define environmental problems and thereby perform research, measure impacts, and find solutions. In this regard, the EPA's National Risk Management Research Laboratory (NRMRL) is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative and defensible engineering basis in support of the EPA's policies, programs, and regulations with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities.

Similar responsibilities have also been assigned to the U.S. Department of Energy (DOE) through the Federal Energy Technology Center (FETC), one of several DOE centers in charge of planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement (IAG) was signed between the EPA and DOE, that made funds available to support the Western Environmental Technology Office and its operating contractor, MSE Technology Applications, Inc. (MSE), as well as Montana Tech of The University of Montana (Montana Tech) for the development of the Mine Waste Technology Program (MWTP).

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Executive Summary

This final report presents data obtained for MWTP Activity IV, Project 3, Photoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Nitrate and Cyanide. Several photoassisted electron transfer reactions were explored for the cleanup of these two mobile toxic constituents commonly found in mine wastewaters. Because nitrate (NO_3^-) exists in a highly oxidized state, only photoreduction experiments were conducted. On the other hand, because cyanide (CN^-) is in a reduced state, only photooxidation experiments were conducted. Each of these processes involved electron transfer reactions with solid photocatalysts or dissolved photosensitizers.

Anatase (titanium dioxide, TiO_2) was the solid photocatalyst for both NO_3^- photoreduction and CN^- photooxidation experiments. Conversely, different reagents were used as dissolved photosensitizers: hydrazine (H_4N_2) and humic acid for NO_3^- photoreduction and hydrogen peroxide (H_2O_2) for CN^- photooxidation. Reaction rates and efficiencies were determined and compared for all experiments. Research involving NO_3^- photoreduction with dissolved photosensitizers appears to be innovative since no published work on the method could be found.

Results show that NO_3^- photoreduction does work; however, under the conditions examined, is not 100% effective. Photoreduction efforts with low amounts of H_4N_2 yielded maximum 12% remediation. When H_4N_2 and TiO_2 were used simultaneously, no remediation was observed. Increased dosage of H_4N_2 and the use of CN^- actually yielded negative remediation efforts. Because H_4N_2 and CN^- are both nitrogen compounds, this behavior was attributed to their oxidation to NO_3^-. Nitrate photoreduction with humic acid worked but was dependent on concentration. The maximum dosage used was 1 gram per liter and yielded a maximum of 21% remediation. Clearly, NO_3^- photoreduction with humic acid was the best technology examined. Because NO_3^- photoreduction was shown to occur, it is considered to be a promising technology and should be examined in more detail in future studies.

By comparison, CN^- photooxidation could be 100% effective but dependent on the conditions applied. Results indicated that it is necessary to control H_2O_2 addition; moderate amounts slowed CN^- photooxidation rates, whereas small and heavy dosages appeared to be okay. Experiments with H_2O_2 were consistently faster than those with TiO_2, and direct photolysis was not plausible. When H_2O_2 and TiO_2 were used simultaneously, remediation was not as good as H_2O_2 alone; this could be attributed to H_2O_2 reduction by TiO_2 and/or the formation of surface complexes between titanium and H_2O_2: $Ti(H_2O_2)^{4+}$ and $Ti(O_2)^{2+}$. Finally, experiments conducted with H_2O_2 in the absence of ultraviolet (UV) radiation (i.e., the Degussa Process) showed better remediation than UV-illuminated TiO_2. This "dark" experiment was not influenced by the presence of TiO_2. Clearly, under the conditions tested, CN^- photooxidation with H_2O_2 as the only reagent yielded the best results. Although this technology is effective, it is also relatively slow (at least under the conditions examined). Consequently, future studies are recommended to enhance the reaction rates. It is important to note that, in this regard, this promising technology has been extended to study metal-complexed cyanides, results of which will be discussed in another report (Ref. 1).

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1. Introduction

This final report was prepared from technical information and validated quality assurance/ quality control (QA/QC) results obtained by Montana Tech of The University of Montana (Montana Tech) for the Mine Waste Technology Program (MWTP), Activity IV, Project 3, Photoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Nitrate and Cyanide. All enclosed materials are followup to approved MWTP Activity IV, Project 3, Work Plan and Quality Assurance Project Plan (QAPP) dated January 1994 and June 1996, respectively (Ref. 2, 3). The information and results are described in accordance with the requirements of the Interagency Agreement (IAG) Activity IV Scope of Work that was signed in June 1991 by the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy (DOE) to initiate work on the MWTP. Furthermore, this MWTP final report addresses the testing and evaluation of promising photolytic technologies for using ultraviolet (UV) radiation to remediate wastewaters containing nitrate (NO_3^-) and cyanide (CN^-) via photoreduction and photooxidation respectively. These toxic constituents were identified in MWTP Activity I Prioritization Reports (Ref. 4-8).

1.1   Relevance to MWTP

Discharge waters from various municipal and industrial operations transport many dissolved chemicals that have adverse effects on the environment and on plant and animal life. For example, dissolved chemicals may leach various heavy metals that would otherwise remain immobile. Aquatic life of all sorts become sick or die due to the toxicity of both the dissolved chemicals and metals. Many wastewater processing technologies that are currently available or being developed emphasize removal of the dissolved chemicals and the heavy metals as cations. The anions associated with metal cations can be equally as toxic but are largely ignored. In this regard, aqueous nitrogen species such as NO_3^-

and CN^- have been recognized as being toxic and their remediation has been considered paramount at several locations in Montana and throughout the United States (Ref. 4-8).

Impetus for this study emanated from the current inability to remediate NO_3^- cost effectively (Ref. 7, 8) and from technical concerns regarding the effectiveness of nonphotolytic CN^--kill processes that have been raised due to the lack of information on the fate of CN^- species and their reaction kinetics and products (Ref. 5, 9). Further impetus comes from concerns of citizens near sites contaminated with NO_3^- and CN^- such as Noranda's Libby Adit Project, Libby, Montana; the Clark Fork River between Deer Lodge and Missoula, Montana; and Chicago Mining Company's heap leach operation, Pony, Montana, to name a few. Nitrate-bearing emissions from Noranda's Libby Adit Project forced development operations to cease (Ref. 10, 11). Likewise, CN^- has been detected in the well water of one Pony resident. Similar problems have been noted for other sites in Montana and throughout the United States (Ref. 4-8). In summary, photolytic technologies have been examined and are discussed in this final report for remediating NO_3^- and CN^-, two mobile toxic constituents that oftentimes are overlooked because they are not cationic heavy metals.

1.1.1   Nitrate

Nitrates are major components in fertilizers and explosives and are common by-products of detonated explosives that contain nitroglycol, nitroglycerin, and nitrocellulose (Ref. 12). Consequently, nitrates predominantly enter discharge waters from the mining and agricultural industries. Nitrates promote the growth of algae and other plant life in slow moving streams, rivers, and lakes resulting in increased turbidity as well as oxygen depletion (Ref. 7, 11). In time, these waterways can become devoid of life (Ref. 13). Excess nitrates in drinking water can cause methemoglobinemia in animals and can be fatal to infants (Ref. 14); NO_3^- is converted into nitrite by

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bacteria within their gastrointestinal tracts. Hemoglobin in the bloodstream reacts with the nitrite instead of oxygen, thereby causing respiratory failure. Nitrate has been removed from solutions using ion exchange, reverse osmosis, and biological methods; however, these methods are expensive and nondestructive—a concentrated waste is produced that must still be treated. Photolysis has therefore been recognized as an excellent possibility for NO_3^- remediation (Ref. 15-21).

1.1.2 Cyanide

Cyanide can be found in solutions as free CN^-, as weak complexes with metals such as cadmium, zinc, and copper, and as strong complexes with other metals, including iron, cobalt, mercury, silver, and gold (Ref. 22). If CN^- is allowed to enter natural waters, it may be ingested by animals and subsequently absorbed by their gastrointestinal and respiratory tracts. The mean lethal dose to the human adult is 50 to 200 milligrams (mg) (Ref. 9). Huiatt et al. (Ref. 9), Wheathington (Ref. 23), and Young et al. (Ref. 24, 25) investigated numerous CN^- treatment technologies using information from literature, industrial, and government sources and noted that oxidation technologies were the only methods that destroyed CN^-. The other technologies, a mix of physical, adsorption, and complexation methods, produced a concentrated waste that required further treatment, as similarly noted above for NO_3^- remediation technologies. Oxidation methods included biological destruction, chemical addition, and photolysis. Biological destruction is used industrially at the Homestake Mine in Lead, South Dakota (Ref. 26, 27); however, research is ongoing at other sites (Ref. 28-33). Numerous sites throughout the world use oxidizing chemicals such as hydrogen peroxide

(H_2O_2) (Ref. 34-37); Caro's acid (H_2SO_5) (Ref. 38-40); sulfur dioxide (SO_2) (Ref. 41-44); and hypochlorite (OCl^-) (Ref. 45-48) to destroy CN^-. Because these oxidative methods were criticized for being unable to treat strong metal complexes, Wheathington (Ref. 23) and Young et al. (Ref. 24, 25) concluded that photolysis could be the most promising method for complete CN^- destruction with the most popular being UV-assisted H_2O_2 (Ref. 21, 49-51) or titanium dioxide (Ref. 21, 50-66).

1.2 Research Objectives

From the above discussions, it is clear that both NO_3^- and CN^- can be remediated by photolysis. Consequently, one aim of this project was to examine the photoassisted remediation of these two mobile toxic constituents. Because NO_3^- exists in a highly oxidized state (i.e., nitrogen is +V), only photoreduction processes were considered for NO_3^- remediation. On the other hand, because nitrogen in CN^- is in a reduced state of -III, CN^- remediation could only be accomplished by photooxidation. Although NO_3^- and CN^- photolytic studies have been reported, especially with solid (i.e., heterogeneous) photocatalysts (Ref. 15-21, 50-66), there appears to be no published work with dissolved (i.e., homogeneous) photosensitizers on NO_3^- and little on CN^-. As a result, the possibility existed that, for the first time, NO_3^- remediation would be accomplished using dissolved photosensitizers. After identifying the appropriate photolytic technology(ies) that could be used for NO_3^- and CN^- remediation, a second goal of the project was to evaluate the most appropriate technology(ies) by determining reaction rates and efficiencies. Ultimately, it was hoped that the appropriate technology(ies) would be developed for immediate transfer to the sites where NO_3^- and CN^- contaminations are known to occur as mentioned above. As a final objective, the appropriate technology(ies) would be recommended for further study(ies).

2. Photochemistry

2.1 Technology Background

Remediation research of polluted waters originating from active or inactive mine sites and associated materials handling procedures has primarily focused on bringing to the affected areas foreign substances and processes that could ultimately disturb a naturally established ecosystem. Remediation methods by, for example, lime addition are inherently expensive and make the sites difficult to revegetate. Overwhelming evidence shows that natural processes occur that heal environmental scars caused by mining activities. These processes include electron transfer reactions that lower the concentrations of mobile toxic constituents in surface and groundwaters via interactions with electromagnetic radiation from the sun, UV radiation in particular. However, these naturally photoassisted processes suffer at night, on cloudy days, and in winter months. During these periods, artificial UV sources are needed to sustain the processes. Furthermore, because the processes may still proceed too slowly, photocatalysts or photosensitizers can be supplemented to absorb and transfer the UV radiant energy to the reactants, thereby remediating the water within more acceptable timeframes. Photocatalysts are predominantly solid semiconductors, and photosensitizers are usually dissolved in solution.

In photolysis, solutions (or other sample types) are irradiated with electromagnetic radiation, usually UV, to promote electron transfer reactions between toxins (i.e., NO_3^- and CN^-) and other available species. The toxins either undergo photoreduction (as with NO_3^-) or photooxidation (as with CN^-) to yield less toxic or nontoxic compounds. Photolysis can be accomplished with direct or indirect techniques. Direct photolysis requires the substance being remediated to absorb the radiation. Indirect processes can be induced by having a second material absorb the radiation and then transfer the photoenergy to the substance being remediated. In this regard, solid semiconductors can be used so they participate only as catalysts (heterogeneous photocatalysis). On the other hand, dissolved photosensitizers can either be consumed during the reaction (homogeneous photolysis) or participate as catalysts (homogeneous photocatalysis). These photoassisted processes are discussed below. However, for simplicity, they will only be discussed as solid photocatalysis and dissolved photolysis.

2.1.1 Solid Photocatalysis

To date, most work has entailed studying the oxidation of toxic organic compounds using solid semiconductors as electron transfer photocatalysts to ultimately produce both carbon dioxide and water (Ref. 65-77). However, current emphasis appears to be on applying this successful technology to the oxidation of inorganic compounds to satisfy new and more stringent environmental regulations. Numerous solid photocatalysts have been reported to work well: TiO_2, ZnO, WO_3, CdS, SiC, Fe_2O_3, and certain zeolites (Ref. 65-68), to name a few. Anatase has been preferred because of its low cost, relative abundance, and high quantum efficiency in converting photon energy into chemical energy (Ref. 50, 52).

For these solid semiconductors to function as electron transfer photocatalysts, their band gap energies must be less than the absorbed UV radiation as determined from the equation:

$$E = h? \qquad\qquad [1]$$

where h is Planck's constant and ? is the frequency of the UV radiation. Upon absorbance, an electron is excited into the conduction band from the valence band where a "hole" is created (see Figure 2.1):
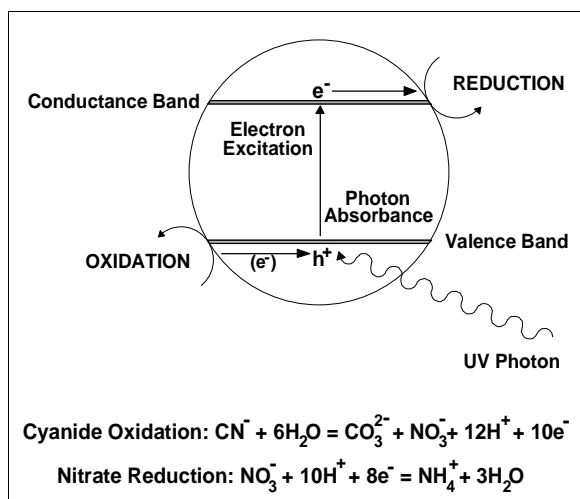
Figure 2.1. Schematic of UV-assisted redox reactions at the surface of solid photocatalysts.

holes to reproduce the reactants. Otherwise no net reaction results.

$$\text{semiconductor} \xrightarrow{h\nu} (e^- \; H^+) \qquad [2]$$
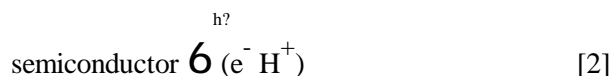
Because the band gap between the conduction and valence band edges lacks energy levels, the excited electron will reside at the conduction band edge whereas the hole will reside at the valence band edge. Consequently, the electron-hole ($e^- \; H^+$) pair will be relatively stable possessing a lifetime that is long enough for electron transfer reactions to occur:

$$H^+ + D \longrightarrow D^+ \qquad [3]$$

$$e^- + A \longrightarrow A^- \qquad [4]$$

Clearly, electron donors (D) become oxidized when the release electrons fill the holes (Reaction 3) and electron acceptors (A) are reduced when they consume the excited electrons (Reaction 4).

Solid electron transfer photocatalysis cannot occur unless both A and D are preadsorbed at the semiconductor surface and the products, D^+ and A^-, do not react with respective excited electrons and

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Furthermore, the Nernst potentials of Reactions 3 and 4 must be thermodynamically favorable. Each of these requirements can be met by (1) using semiconductors that are amenable to the adsorption of both A and D but not A^- and D^+, (2) choosing a semiconductor whose band gap is appropriate for the electron transfer reactions to occur, (3) choosing ligands that react with the radical products to form inert species, (4) selecting appropriate pH conditions, (5) stirring/ bubbling the system to remove the radical products from the surface, (6) depositing metals (i.e., platinum) at the surface as a co-catalyst to localize the excited electrons, and (7) promoting reactions between the radical products themselves. Clearly, the surface, electro-, solution, and analytical chemistries of the solid electron transfer photocatalytic reactions must be well understood before they can be induced and/or enhanced.

As already stated, solid photocatalysis has primarily been used to examine the oxidation of toxic organic compounds (Ref. 65-77); however, the oxidation of inorganic compounds is currently receiving much attention (Ref. 50-66). In addition, it is important to further note that the photoreduction of both organic and inorganic compounds is possible (Ref. 15-21, 51, 65-68, 73) but is less frequently observed presumably because the reducing power of the excited electron is significantly lower than the oxidizing power of the hole and because the compounds must kinetically compete with oxygen and/or water as the electron acceptor (Ref. 73).

2.1.2 Dissolved Photolysis

Photochemical reactions in the absence of solid semiconductors have involved both organic and inorganic compounds and have been classified as either direct or indirect processes. In direct photochemical processes, the compound (designated as X in subsequent equations) absorbs the electromagnetic radiation to form an excited 4state that then reacts to form a variety of products (see Figure 2.2):
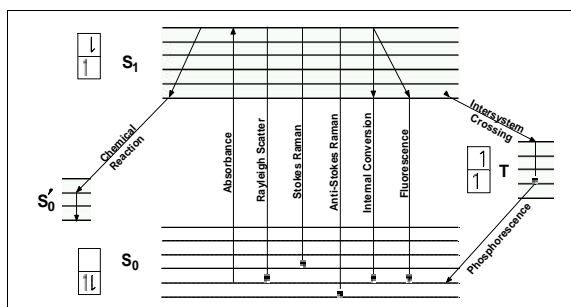
Figure 2.2. Jablonski energy-level diagram depicting a direct UV-assisted chemical reaction.

$$X + h? \rightarrow X^* \rightarrow products \qquad [5]$$

For most organic compounds, this reaction is typical of decompositions. For certain inorganic compounds, this reaction either (1) yields changes in oxidation states or (2) transfers the photoenergy to water yielding hydroxyl radicals (OH) that can then decompose various organic compounds or react with other inorganic species to produce specific radicals (Ref. 50, 65-69). With indirect photochemical processes, photosensitizers absorb the radiation

$$S + h? \rightarrow S^* \qquad [6]$$

and then transfer the photoenergy to the compound, thereby catalyzing the following reaction:

$$S^* + X \rightarrow S + X^* \rightarrow S + products \qquad [7]$$
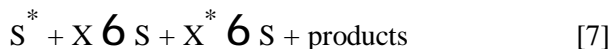
or transfer the energy to another species (usually oxygen) to induce the following reactions:

$$S^* + O_2 \rightarrow O_2^* + S \rightarrow products + S \qquad [8]$$
$$O_2^* + X \rightarrow products \qquad [9]$$
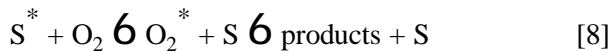
where the oxygen radical may participate as either a reactant or a cocatalyst. In some cases, the photosensitizer (S) is consumed in the process and

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is therefore not considered to be a dissolved photocatalyst.

Each of the radicals mentioned above (i.e., inorganic, organic, hydroxyl, specific, photosensitizer, and oxygen) are dissolved photocatalysts and can induce oxidation (electron donating) or reduction (electron accepting) reactions in the same manner as solid photocatalysts. However, the dissolved photocatalysts are not dependent on adsorption and other surface area phenomenon and, by comparison, can therefore be expected to enhance reaction rates by orders of magnitude, dependent only on the concentration of the dissolved photocatalyst. Other dissolved photocatalysts include photon-active redox couples where the oxidant would be the electron donor and the reductant would be the electron acceptor.

2.2 E_H-pH Diagrams

Because photolysis involves electron transfer reactions, it is helpful to examine thermodynamic equilibrium diagrams such as E_H-pH diagrams to see what possible reactions may occur between reacting species and to see what products my be formed as the reaction occurs. In this regard, E_H-pH diagrams were generated using STABCAL (Ref. 78, 79). STABCAL is a program developed for IBM-compatible personal computers to calculate various types of thermodynamic stability diagrams. To construct the diagrams for NO_3^-, CN^-, and TiO_2, thermodynamic data at 298 K was obtained from National Bureau of Standards' tables from a reference library within the STABCAL program.

2.2.1 Nitrate

Presented in Figure 2.3 is an E_H-pH diagram for nitrogen. Nitrate is shown to be predominantly stable at high oxidation potentials and is partially within the stability region of water delineated by the long-dashed lines. Nitrate remediation must therefore occur by reduction. This can conceivably occur via nitrite or ammonia production:

Figure 2.3. Nitrogen E_H-pH diagram illustrating nitrate reduction to nitrite and ammonia. (Shaded region depicts the band gap of anatase.)

$$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O \qquad [10]$$

$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O \qquad [11]$$
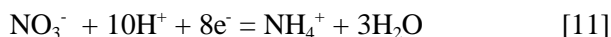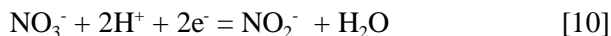
However, nitrite and ammonia are also very stable in water and are considered to be more toxic than NO_3^- (Ref. 14).

Because nitrogen gas possesses a high strength triple bond and is thus inert and relatively insoluble in water (Ref. 82), it would ultimately be desirable to produce nitrogen gas:

$$NO_3^- + 6H^+ + 5e^- = \frac{1}{2}N_2(g) + 3H_2O \qquad [12]$$
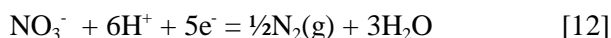
In this case, the nitrogen oxidation state changes from +V (NO_3^-) to 0 (nitrogen gas) as opposed to +III (nitrite) and -III (ammonia). When nitrogen gas is considered in the calculation of E_H-pH diagrams, it dominates much of the water stability region as revealed in Figure 2.4. Separate steps for the remediation of nitrite and ammonia would therefore be avoided. Similar reactions could also be determined for the formation of nitrous oxide (NO) gas (+II) and nitrogen dioxide (NO_2) gas (+IV), etc.; however, these products would also require additional remediation.
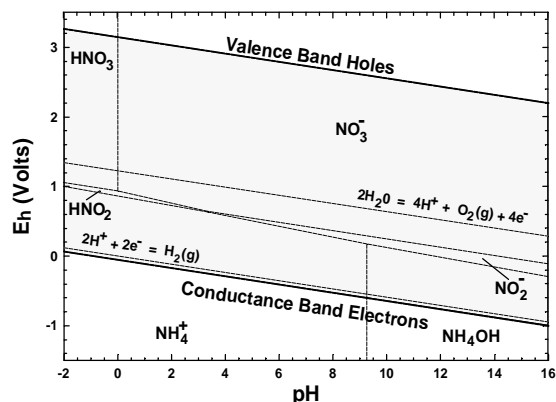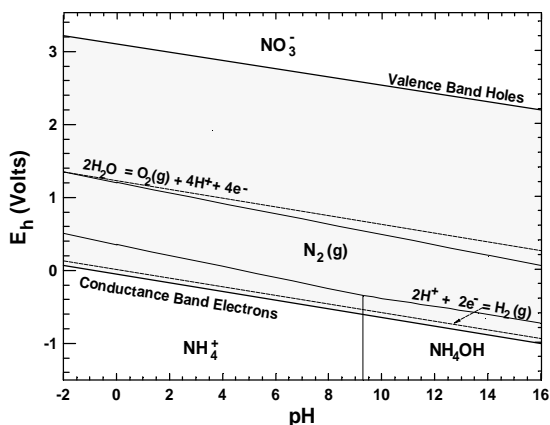
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Figure 2.4. Nitrogen E_H-pH diagram illustrating nitrate reduction to nitrogen gas and ammonia. (Shaded region depicts the band gap of anatase.)

2.2.2 *Cyanide*

An E_H-pH diagram for CN^- at 1×10^{-2} molar (M) and 298 K is illustrated in Figure 2.5. Cyanide is depicted to be predominantly stable at pH values greater than 9.23 and at E_H values just below the stability of water. In this regard, water should directly oxidize CN^- to form cyanate (OCN^-):

$$CN^- + H_2O = OCN^- + 2H^+ + 2e^- \qquad [13]$$
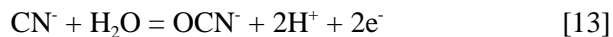
However, the reaction is slow because a large activation energy must first be overcome (Ref. 9). In this regard, it is important to note that photolysis helps overcome this energy barrier. The liberation of hydrogen cations (H^+) as depicted in Reaction 13 substantiates a precaution that pH-control is necessary to avoid toxic hydrogen CN^- gas formation and evolution. The E_H-pH diagram further predicts that continued oxidation should yield various nitrite (NO_2^-) and carbonate (CO_3^{2-}) species and eventually produce NO_3^-:

$$OCN^- + 4H_2O = NO_2^- + CO_3^{2-} + \\ 8H^+ + 6e^- \qquad [14]$$

$$NO_2^- + H_2O = NO_3^- + 2H^+ + 2e^- \qquad [15]$$
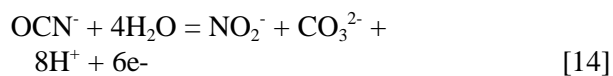
However, Reactions 14 and 15 are also hindered by slow reaction rates even in the presence of aerated or oxygenated solutions (Ref. 9). Previous investigations (Ref. 83, 84) constructed E_H-pH diagrams for various CN^- metal water systems but did not consider nitrites, nitrates, and carbonates as oxidation products. In this regard, this study marked the first time that such species were considered as reaction products for incorporation into CN^- E_H-pH diagrams.

2.2.3 *Anatase*

Reactivities for electron-hole pairs produced at TiO_2 surfaces were superimposed on the E_H-pH diagrams presented for NO_3^- and CN^- in Figures 2.3-2.5. A comparison to Figure 2.1 shows that the valence and conductance bands are reversed; however, this is merely due to convention. The position of the bands concurs with those determined at pH 1, 7, and 14 and illustrates that the bandgap for TiO_2 is 3.2 electron volts (eV) (Ref. 65-68). According to Equation 1, a photon must have a frequency of 7.75×10^{14} hertz for its absorbance to occur. This equates to a maximum wavelength of 387.5 nanometers (nm), indicating that the 254 nm UV sources employed in this study was adequate for inducing solid photocatalysis (see Section 3, Treatability).
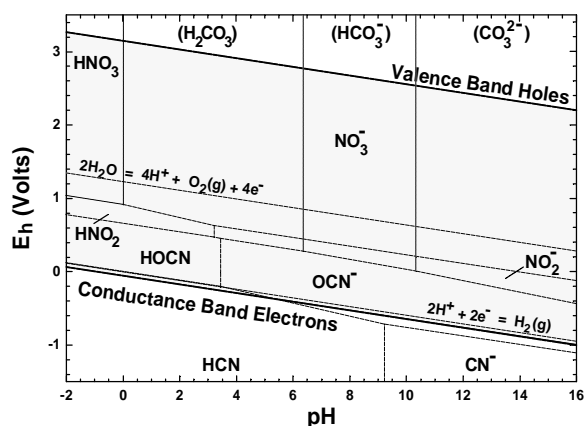
Figure 2.5. Carbon-Nitrogen E_H-pH diagram in the absence of nitrogen gas illustrating cyanide oxidation to cyanate, nitrite, and nitrate. (Shaded region depicts the band gap of anatase**.)**

As previously noted, conductance and valence bands represent the affinity for electrons to be consumed (by holes) and donated (as excited electrons) and are therefore a measure of relative reduction and oxidation potentials, respectively. Because NO_3^- and nitrite species lie above the conductance band, they can undergo reduction, as depicted in Reactions 10 through 12, by accepting photon-excited electrons Similarly, since the predominant stability regions for CN^-, cyanate, and nitrite lie below the valence band, they can undergo oxidation, as depicted in Reactions 13 through 15, by releasing electrons to photon-produced holes.

3. Treatability

Experimental procedures were essentially the same for NO_3^- photoreduction and CN^- photooxidation experiments. The only difference were the reagents that were used.

3.1 General Test Procedures

Sample solutions of 200 milliliters (mL) were prepared in standard 250-mL Pyrex beakers (Fisher) using deionized/distilled (DI) water with either reagent-grade sodium nitrate (J.T. Baker) or sodium CN^- (Coleman and Bell) at 1×10^{-3} M and 1×10^{-2} M, respectively (see Section 6, Field Samples). These concentrations are respectively equivalent to 62.5 parts per million (ppm) NO_3^- and 260 ppm CN^- and are approximate averages of typical concentrations observed in literature searches of mine wastewaters. After inserting Teflon-coated magnetic stirbars (VWR) in the solutions, the beakers were placed on magnetic stirrers (VWR) operating at approximately 2-speed and positioned in a chemical hood directly below UV sources (UVP, Inc.) with rated intensities of 600 microwatt per square centimeter ($\mu W/cm^2$). The UV sources emitted radiation at wavelengths between 150 nm and 280 nm with a peak intensity centered at 254 nm. Tests were conducted in the absence and presence of various concentrations of reagent-grade photochemicals: H_2O_2 (J.T. Baker); hydrazine (H_4N_2) (J.T. Baker); and humic acid (J.T. Baker) as dissolved photosensitizers and TiO_2 (Degussa P25) as the solid photocatalyst. Figure 3.1 depicts the experimental setup.

QA/QC procedures were conducted at all times (see Ref. 3; Section 4, QA/QC; and Section 6, QA/QC Activities). Reagent schedules for the 13 UV-catalyzed QA/QC experiments are listed in Table 3.1. These experiments were found to be the most desirable after determining that the most appropriate photolytic technologies involved dissolved photosensitizers and solid photocatalysts as suggested by resulting publications from this project, including the thesis
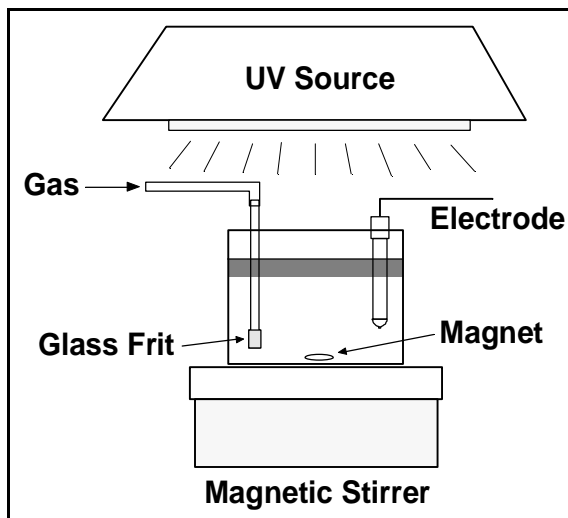
Figure 3.1. Experimental setup for nitrate photoreduction and cyanide photooxidation tests.

of a Master's student who graduated in Metallurgical Engineering (Ref. 21, 24, 25, 85, 86).

3.1.1 Nitrate

For NO_3^- photoreduction experiments, solutions were maintained near pH 10 using HCl (Fischer) and NaOH (Fischer) as needed and in conjunction with an Orion pH electrode (Model 81-02) and meter (Model 920A). The solutions were continuously sparged with argon gas to eliminate oxygen. At times measured by a stopwatch and determined by reaction rates, 1 mL aliquot samples were taken with syringes (Fischer) equipped with 0.3-micron filters (Fischer). The aliquots were then injected into a Dionex DX-100 ion chromatograph (Model DX 1-03) equipped with an IONPAC® AS4A analytical column (P/N 37041), an IONPAC® AG4A guard column (P/N 30742), and an ion self-suppressor (P/N 43189) for measuring NO_3^- and nitrite concentrations. Because ion chromographic measurements take 5 minutes to accomplish, many aliquot samples were stored temporarily in 20-mL plastic vials (Fischer). Typical experiments were conducted for 3 hours.

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Table 3.1   UV-irradiated nitrate and cyanide test solutions and reagent schedules

Sample No.	Sample Reagent Concentration (M)		Photolytic Reagent Concentration (M or g/l)		Sparging Gas
1	Nitrate	0.001 M	Humic Acid	0.2 g/l	Ar
2	Nitrate	0.001 M	Humic Acid	0.6 g/l	Ar
3	Nitrate	0.001 M	Humic Acid	1.0 g/l	Ar
4	Nitrate	0.001 M	Hydrazine	0.2 M	Ar
5	Nitrate	0.001 M	Hydrazine	2.0 M	Ar
6	Nitrate	0.001 M	Hydrazine TiO_2	0.2 M 1.5 g/l	Ar
7	Nitrate	0.001 M	Cyanide	0.001 M	O_2
8	Cyanide	0.01 M	None		O_2
9	Cyanide	0.01 M	30% H_2O_2	0.5 ml	O_2
10	Cyanide	0.01 M	30% H_2O_2	1.0 ml	O_2
11	Cyanide	0.01 M	30% H_2O_2	5.0 ml	O_2
12	Cyanide	0.01 M	TiO_2	1.5 g/l	O_2
13	Cyanide	0.01 M	30% H_2O_2 TiO_2	1.0 ml 1.5 g/l	O_2

3.1.2 Cyanide

For CN^- oxidation experiments, solutions were maintained at pH 11 using HCl and NaOH and in conjunction with the same Orion pH electrode and meter as listed above. The solutions were continuously sparged with oxygen gas to maximize oxidizing conditions and prevent pH drop due to the progression of the photooxidation reactions (see Reactions 13-15). Cyanide concentrations were measured using an Orion CN^- electrode (Model 94-06) coupled to an Orion reference electrode (Model 90-02 res) and the previously mentioned pH meter. This was a necessary precaution to ensure toxic hydrogen cyanide (HCN) gas was not evolved. Aliquots were also taken to measure for the appearance of NO_3^- and nitrite using the IC procedure described

above. Typical experiments were conducted for 5 hours. Experiments were also conducted in the dark to assess the applicability of UV radiation (see Table 3.2).

3.2 Experimental Results

Nitrate photoreduction data is listed in Appendix A. To present the data with clarity, all data points collected in a test were corrected by subtracting or adding a constant such that the initial concentration for all tests was 62.5 ppm NO_3^-. Corresponding results are illustrated in Figures 3.2-3.3. Cyanide photooxidation data is listed in Appendix B. For this data, no corrections for clarity were needed. Results are illustrated in Figures 3.4-3.6. All results are discussed in the ensuing sections.

Table 3.2   Non-UV-irradiated cyanide test solutions and reagent schedules.

Sample No.	Sample Reagent Concentration (M)		Photolytic Reagent Concentration (M or g/l)		Sparging Gas
14	Cyanide	0.01 M	30% H_2O_2	1.0 ml	O_2
15	Cyanide	0.01 M	30% H_2O_2 TiO_2	1.0 ml 1.5 g/l	O_2
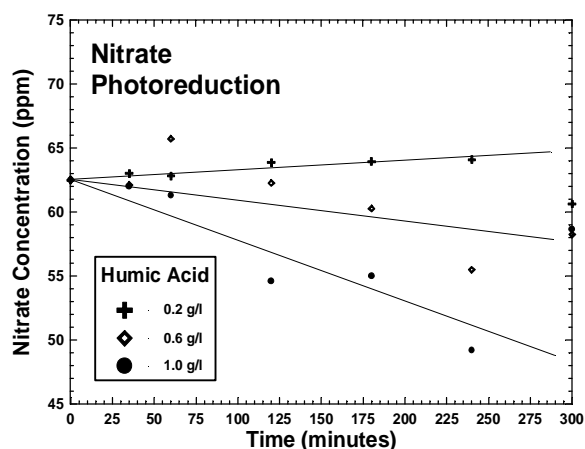
Figure 3.2. Effect of humic acid concentration on nitrate photoreduction.
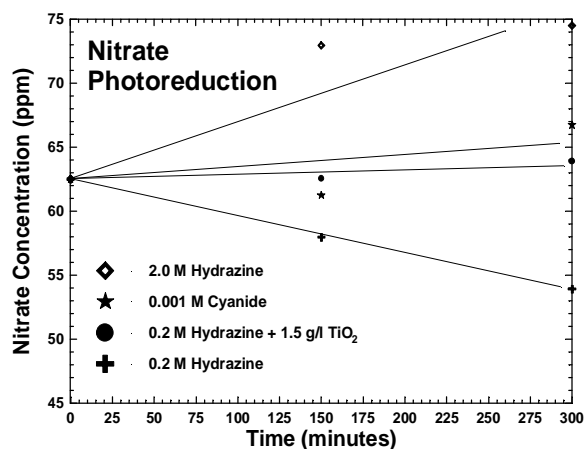
Figure 3.3. Effect of nitrogen-bearing photochemicals on nitrate photoreduction.
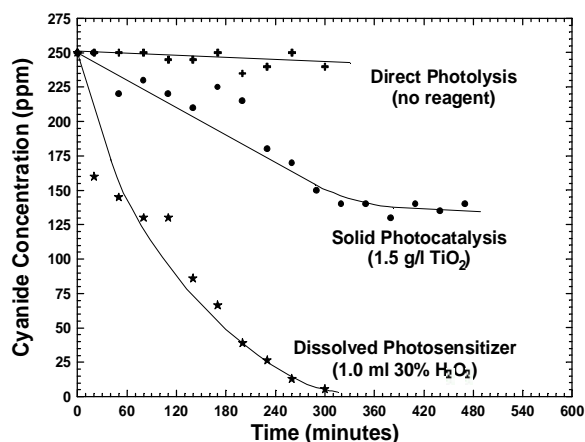
Figure 3.4. Effect of photolytic process on cyanide photooxidation.
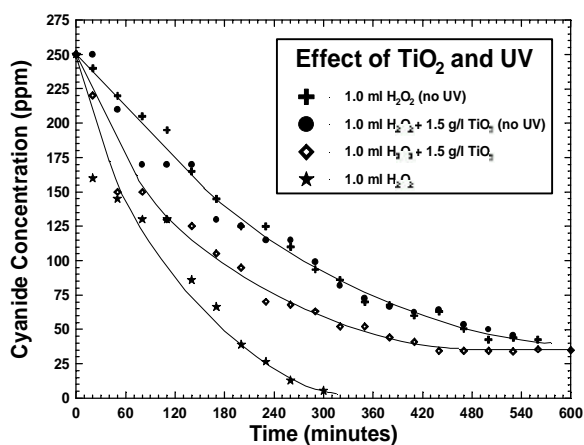
Figure 3.5. Effect of hydrogen peroxide concentration on cyanide photooxidation.
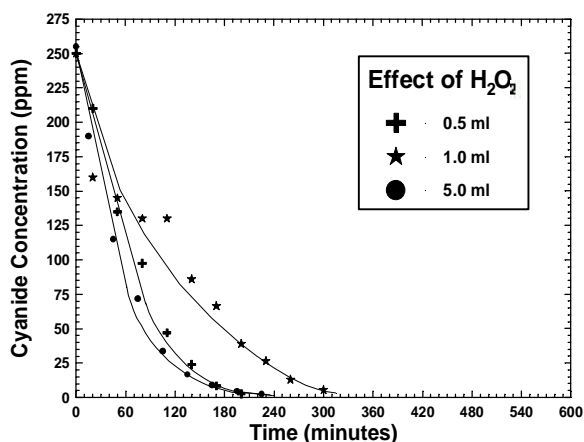
Figure 3.6. Effect of anatase and UV on cyanide oxidation.

3.2.1 Nitrate Photoreduction

Nitrate photoreduction results obtained with humic acid are shown in Figure 3.2. The results show that photoreduction did not occur with 0.2 grams per liter (g/L) humic acid and may even have generated additional NO_3^-. In this regard, it is important to note that the humic acid is a high molecular weight organic of unknown composition and may contain nitrogen that oxidized to NO_3^-. However, larger quantities of humic acid yielded increasing levels of NO_3^- remediation: 0.6 and 1 g/L gave approximately 12 and 21% conversion, respectively. The scatter in the data is believed to

be caused by a nitrite product (photo)oxidizing back to NO_3^-.

Photoreduction experiments were also conducted with H_4N_2, CN^-, and TiO_2. Results plotted in Figure 3.3 show that these chemicals do not work well; only 0.2 M H_4N_2 worked although minimally yielding approximately 13% NO_3^- photoreduction. Increased H_4N_2 concentration to 2.0 M yielded negative remediation as observed for the low concentration of humic acid. H_4N_2 is a nitrogen-containing compound and could easily have photooxidized to NO_3^-. Similar observations were observed for the experiment involving CN^-, another nitrogen compound. Likewise, the H_4N_2/TiO_2 experiment yielded negative results. A comparison to the 0.2 M H_4N_2 experiment indicates that TiO_2 is detrimental to the use of H_4N_2 as a photoreductant by most likely causing its (photo)oxidation.

This study showed that NO_3^- photoreduction is possible with humic acid and H_4N_2. Both photosensitizers were dependent on concentration. With increasing humic acid or decreasing H_4N_2, NO_3^- photoreduction was better. However, remediation levels never exceeded 21% presumably because NO_3^- photoreduction only proceeded as far as nitrite formation, which reversibly photooxidized back to NO_3^-. Nitrogen gas production would have been better since such reversibility would have been avoided. In this regard, further research is recommended.

3.2.2 Cyanide Photooxidation

Different photolytic processes for CN^- photooxidation were conducted as shown in Figure 3.4. Results show that CN^-, when exposed to UV radiation in the absence of any reagent (i.e., direct photolysis), does not quickly photooxidize; only a maximum of 4% remediation was observed in 5 hours. By comparison, solid photocatalysis with 1.5 g/L TiO_2 yielded approximately 50% CN^- photooxidation, and photolysis with 1 mL 30% H_2O_2 yielded over 99% CN^- photooxidation in the same timeframe. Clearly, the preferred method, under the chosen conditions, is H_2O_2 photolysis.

In Figure 3.5, the 1-mL H_2O_2 experiment is plotted again and compared to several other advanced oxidation techniques to demonstrate the utility of UV-irradiation. By comparison, when 1 mL 30% H_2O_2 was added and no UV radiation was used (i.e., the Degussa Process or "dark" reaction), only 84% remediation was achieved in 9 hours. This exact same level of remediation resulted when, without UV exposure, TiO_2 was also added, which is expected since TiO_2 is inert in the absence of UV radiation. However, when the UV source was turned on, the CN^- was observed to oxidize to approximately 90% remediation in 7 hours. Since the H_2O_2/TiO_2 UV-experiment did not perform as well as the H_2O_2-only experiment, it is clear that TiO_2 is deleterious to CN^- photooxidation with H_2O_2. This can be attributed to H_2O_2 being photoreduced by the TiO_2. Similarly, it was earlier suggested that H_4N_2 was photooxidized by TiO_2. In addition, it is also conceivable that titanium-H_2O_2 complexes such as $Ti(H_2O_2)^{4+}$ and $Ti(O_2)^{2+}$ (Ref. 87) formed to minimize the effect of CN^- photooxidation.

Finally, Figure 3.6 is presented to illustrate the effect of H_2O_2 on CN^- photooxidation. The results show that decreased and increased dosages of 0.5 and 5 mL improved CN^- remediation to >99% in 3.5 hours. This behavior suggests there is a strong dependency on H_2O_2 concentration such that moderate amounts (1 mL) are not as good as low (0.5 mL) and high (5 mL) and could be attributed to speciation phenomenon brought on by E_H changes.

This study showed that CN^- photooxidation was not possible without adding reagents such as TiO_2 as a solid photocatalyst and H_2O_2 as a dissolved photosensitizer. Anatase hindered CN^- photooxidation processes in the presence of H_2O_2 presumably because TiO_2 photoreduced the H_2O_2 or because titanium complexed with the H_2O_2. In all cases, when H_2O_2 was used alone, near-100% CN^- remediation resulted. However, H_2O_2 photosensitization was found to be inexplicably dependent on concentration; moderate additions did

not perform as well as low and high additions. In this regard, further research is also recommended.

3.3 Summary

Results showed that NO_3^- photoreduction worked; however, under the conditions examined, it was not 100% effective. Photoreduction efforts with low amounts of H_4N_2 yielded maximum 12% remediation. When H_4N_2 and TiO_2 were used simultaneously, no remediation was observed. Increased dosage of H_4N_2 and the use of CN^- actually yielded negative remediation efforts. Because these are both nitrogen compounds, this behavior was attributed to their oxidation to NO_3^-. Nitrate photoreduction with humic acid worked but was dependent on concentration. The maximum dosage used was 1 g/L and yielded a maximum of 21% remediation. Clearly, NO_3^- photoreduction with humic acid was the best technology examined. Because NO_3^- photoreduction was shown to occur, it is considered to be a promising technology and should be examined in more detail in future studies.

By comparison, CN^- photooxidation could be 100% effective but dependent on the conditions applied. Results indicated that H_2O_2 addition is necessary for control. Moderate amounts slowed CN^- photooxidation rates whereas small and heavy dosages appeared to be okay. Experiments with H_2O_2 were consistently faster than those with TiO_2. Direct photolysis was not plausible. When H_2O_2 and TiO_2 were used simultaneously, remediation was not as good as H_2O_2 alone. This could be attributed to H_2O_2 reduction by TiO_2 and/or the formation of surface complexes between titanium and H_2O_2: $Ti(H_2O_2)^{4+}$ and $Ti(O_2)^{2+}$. Finally, experiments conducted with H_2O_2 in the absence of UV radiation (i.e., the Degussa Process) showed better remediation than UV-illuminated TiO_2. This "dark" experiment was not influenced by the presence of TiO_2. Clearly, under the conditions tested, CN^- photooxidation with H_2O_2 as the only reagent yielded the best results. Although this technology is effective, it is also relatively slow (at least under the conditions examined). Consequently, future studies are recommended to enhance the reaction rates. It is important to note that, in this regard, promising technology has been extended to study metal-complexed cyanides of which QA/QC results will be discussed in another final report (Ref. 1).

4. QA/QC

Major purposes of this MWTP project were identifying photolytic processes that could be used for the remediation of NO_3^- and CN^- in wastewaters and evaluating the processes to assess their scientific feasibility via determining reaction kinetics and products so that recommendations could be made to continue this research effort. The programmatic and regulatory setting in which the project QA was conducted was Category III as outlined in MWTP Activity IV, Project 3 QAPP (Ref. 3). Projects are designated Category III when results are used to evaluate and select basic options or to perform feasibility studies or preliminary assessments of unexplored areas. Existing background data presented in Section 2, Photochemistry, was not required to conform to any criteria. This information is considered common knowledge since it was predominantly the foundation to the work plan (Ref. 2).

4.1 QA/QC Objectives

The QA/QC objectives outlined for the project were specified to generate acceptable data. The MWTP Activity IV, Project 3 QAPP (Ref. 3) was provided to ensure:

- measurements were appropriate for achieving project objectives;
- QC procedures were sufficient for obtaining data of known and adequate quality; and
- such data would be defensible if technically challenged.

Ultimately, it would be desirable to show that the selected photolytic technologies for NO_3^- and CN^- remediation yielded concentrations below the EPA Drinking Water Standards of 10 ppm/$1.6x10^{-4}$ M NO_3^- (Ref. 8) and 200 parts per billion (ppb)/$7.7x10^{-6}$ M CN^- (Ref. 22). However, as noted for the NO_3^- photoreduction experiments, NO_3^- remediation levels did not exceed 21% and consequently did not meet the

EPA Drinking Water Standard. Likewise, because a CN^--specific ion electrode with a detection limit of $8x10^{-6}$ M was used, quality-assured measurements below the Drinking Water Standard could not be determined. Nevertheless, project objectives were to identify and evaluate appropriate photolytic processes that remediate NO_3^- and CN^- in wastewaters not necessarily achieve the drinking water standard. This task would be reserved for future studies and accordingly recommended if such concentrations were obtained.

4.2 Analyses

Nitrate and CN^- solutions were monitored for pH as well as NO_3^-, nitrite, and CN^- concentrations, where appropriate. Only EPA-approved methods were employed.

4.2.1 U.S. EPA procedures

EPA-approved methods included pH Electrometric Measurement (Method No. 4500-H^+), Determination of Inorganic Anions in Water by Ion Chromatography (Method No. 300.0) for the nitrite and NO_3^- concentration measurements, and Cyanide Selective Electrode Measurement (Method No. 4500-CN-F-modified). Both electrometric measurements for pH and CN^- concentration were conducted in the reaction vessel at times measured by stopwatch and determined by reaction kinetics. The pH was controlled at pH 10 for NO_3^- photoreduction experiments and pH 11 for CN^- oxidation experiments using drops from HCl and NaOH solutions, as needed. Nitrite and NO_3^- concentrations were determined by injecting 1-mL aliquot samples into the ion chromatograph after having been taken at times measured by stopwatch and determined by reaction kinetics and having been stored temporarily in 20-mL plastic vials between measurements. Equipment manufacturers and types are specified in Section 3, Treatability.

4.2.2 Calibrations

pH meter. Buffer solutions at pH 7 and 11 were used in the standard two-point calibration of the pH meter. The buffer pH values bracketed the pH 10 and pH 11 controls that were used for the NO_3^- and CN^- experiments, respectively. The pH meter was recalibrated after every 20 measurements and at the conclusion of every test. Percent slopes were consistently found to be $100 \pm 5\%$. Measurements of pH were noncritical to all tests.

Ion chromatograph. Before every test, a blank and three nitrite and NO_3^- standards were used to establish working curves between 0 and 250 ppm. This calibration range bracketed all NO_3^- and nitrite concentrations measured for the NO_3^- photoreduction and CN^- photooxidation tests. Calibration curves were analyzed by PeakSimple data software (SRI Instruments) using R^2-correlation coefficients. In this regard, R^2-values typically measured 0.97, which was consistently greater than the 0.90 acceptance criterium. Although never encountered, the chromatograph

was to be recalibrated if a standard, upon being checked after every 20th measurement, was outside 75-125% recovery. Nitrite and NO_3^- measurements were critical to all tests.

Cyanide electrode. The EPA-approved Cyanide Selective Electrode Measurement Method was modified to a three-point calibration using a working curve from 2.5 to 250 ppm CN^- from the four-point calibration with a working curve from 0.025 to 2.5 ppm CN^-. This calibration range bracketed most CN^- concentrations as the tests were allowed to progress; only in one case was the initial concentration outside the calibration range, although just barely (260 ppm). Slope values were recorded in millivolts (mV) and consistently found to be within acceptable criteria of 59.2 ± 7 mV. Although never encountered, the CN^- electrode was to be recalibrated if a standard, upon being checked after every 5th measurement, was outside 95-105% recovery of the standard concentration. Cyanide measurements were critical to all CN^- tests.

5. Synthetic Test Samples

Synthetic wastewaters were used in this study in place of actual field samples. Cyanide and nitrate solutions were made using DI water and reagent grade chemicals at 1×10^{-2} M and 1×10^{-3} M, respectively.

These concentrations are equivalent tp 260 ppm CN^- and 62.5 ppm NO_3 and are approximate averages of concentrations observed in mine wastewaters according to the literature.

6. QA/QC Check Procedures

Numerous procedures were in place to ensure quality data was reported. These QC check procedures included:

- recalibrating the various instruments used through the course of the tests as described in Section 4, QA/QC;
- analyzing calibration standards periodically to ensure the various instruments were functioning properly as also described in Section 4, QA/QC;
- measuring reagent blanks periodically to ensure the various instruments were not contaminated, thereby giving false readings;
- running a duplicate sample to ensure the data was reproducible;
- running a second duplicate sample in the dark to verify effects of UV radiation;
- matrix-spiking a test to ensure the various instruments were functioning properly, thereby yielding results within 75-125% recovery;

- using laboratory-fortified blanks for determining acceptable performance of the ion chromatograph; and
- establishing proficiency on the ion chromatograph by measuring four equally prepared aliquots, calculating average percent recoveries, standard deviations, and upper and lower control limits, and by comparing results to values found in the accuracy and precision table found in Determination of Inorganic Anions in Water by Ion Chromatography (Method No. 300.0).

Because all QA/QC check procedures passed, no corrective action was taken for any of the NO_3^- photoreduction and CN^- photooxidation tests conducted in this study.

7. Conclusions

7.1 Summary

Results show that NO_3^- photoreduction does work; however, under the conditions examined, it is not 100% effective. Photoreduction efforts with low amounts of H_4N_2 yielded maximum 12% remediation. When H_4N_2 and TiO_2 were used simultaneously, no remediation was observed. Increased dosage of H_4N_2 and the use of CN^- actually yielded negative remediation efforts. Because H_4N_2 and CN^- are both nitrogen compounds, this behavior was attributed to their oxidation to NO_3^-. Nitrate photoreduction with humic acid worked but was dependent on concentration. The maximum dosage used was 1 g/L and yielded a maximum of 21% remediation. Clearly, NO_3^- photoreduction with humic acid was the best technology examined.

By comparison, CN^- photooxidation could be 100% effective but dependent on the conditions applied. Results indicated that H_2O_2 addition is necessary for control. Moderate amounts slowed CN^- photooxidation rates, whereas small and heavy dosages appeared to be okay. Experiments with H_2O_2 were consistently faster than those with TiO_2, and direct photolysis was not plausible. When H_2O_2 and TiO_2 were used simultaneously, remediation was not as good as H_2O_2 alone. This could be attributed to H_2O_2 reduction by TiO_2 and/or the formation of surface complexes between titanium and H_2O_2: $Ti(H_2O_2)^{4+}$ and $Ti(O_2)^{2+}$. Finally, experiments conducted with H_2O_2 in the absence of UV radiation (i.e., the Degussa Process) showed better remediation than UV-illuminated TiO_2. This "dark" experiment was not influenced by the presence of TiO_2. Clearly, under the conditions tested, CN^- photooxidation with H_2O_2 as the only reagent yielded the best results. Although this technology is effective, it is also relatively slow (3.5 hours under the conditions examined).

7.2 Recommendations

Nitrate photoreduction was shown to occur but only yielded a maximum of 20% remediation. Cyanide photooxidation could yield 100% remediation but was rather slow. Clearly, both of these technologies are promising but require further investigation to improve upon reaction efficiencies and/or reaction rates. Different research areas would include examining other solid photocatalysts, dissolved photosensitizers, NO_3^- and CN^- starting concentrations, sparging gases, temperatures, pH conditions, UV wavelengths, and UV intensities. ZnO, WO_3, CDs, SiC, Fe_2O_3, and certain zeolites, for examples, would be interesting photocatalysts to study. Formate and oxalate could be interesting photosensitizers for examining. CH_4, CO, H_2, O_3, and CO_2 are excellent candidates for changing atmospheric conditions. Temperatures ranging from near freezing to near boiling should be examined to mimic changing conditions observed in cold and hot climates. Finally, in this study, the UV wavelength and intensity was restricted to 254 nm and 600 ⲫW/cm². Other wavelengths and intensities are available and can be obtained from a variety of different sources including lamps, arcs, and lasers. Most of these options should be done and are therefore recommended for further study.

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Appendix A
Nitrate Data

Appendix B
Cyanide Data